Chapter 9

Summary and Outlook

The aim of the present thesis was to establish a first methodological access to a first-principles based treatment of a prominent defect like atomic steps at single-crystal surfaces, when the latter are exposed to realistic gaseous environments. This methodological work was illustrated and carried out using an oxygen gas-phase and the close-packed (111) step at Pd(100) as example. Specific conclusions, also on the physics regarding this model system, were already presented at the end of each chapter, which is why we restrict this final chapter to an outlook of only the methodological aspects.

Addressing a defect at a metal single-crystal facet exposed to a gaseous environment requires to combine two, somehow conflicting aspects, even if only targeting a situation in thermodynamic equilibrium. In order to obtain a reliable energetics one needs to resort to first-principles electronic structure calculations, nowadays typically achieved using density-functional theory. In order to properly account for entropic effects at finite temperatures one needs to evaluate the partition function, nowadays *e.g.* with Monte Carlo techniques. Even though the latter enable already a most efficient sampling, they still typically need a number of total energy evaluations that far exceeds present day computational facilities. At metal surfaces this is particularly pronounced since large (and thus highly expensive) supercell calculations are required to capture the metallic band structure at the extended surface. While this makes already the treatment of entropic effects at ideal single-crystal surfaces highly challenging, one has to resort to even much larger supercell calculations of vicinal surfaces to capture an extended defect like atomic steps within the underlying periodic boundary condition framework.

In the present thesis we therefore employed an intermediate step in form of a coarse-grained lattice-gas Hamiltonian. Once parameterized with first-principles data from the supercell calculations, the algebraic form of the LGH allows easily for the manifold of total energy evaluations required in the statistical simulations. The crucial aspects in this approach are then the parameterization of the LGH, and for the aspired predictive character of the theory how the uncertainties in the underlying electronic structure calculations propagate to the mesoscopic simulation results. We showed how both aspects can be systematically addressed in the case of the ideal Pd(100)

surface. The increased complexity when also accounting for the step forced us already to a much less rigorous approach there. The significantly increased number of lateral interactions makes checks on the truncated LGH more cumbersome and dictates also a significantly larger number of large supercell calculations. While conceptually straightforward, the approach gets therefore more and more limited in practice when moving to ever more complex scenarios, *e.g.* co-adsorption in mixed environments or a coexistence of various defects like steps, vacancies or facet edges. This is not to mention the complications that would come into play, if the gaseous environment would lead to structural rearrangements beyond the simple adlayer formation addressed here.

In this respect, our finding that most of the error due to the approximate DFT exchange-correlation functional only propagates to the on-site energy and most short-ranged lateral interactions could indicate an intriguing possibility. If this finding is indeed of more general nature, it suggests than one could *e.g.* only use a lower level treatment to determine most of the increasing number of lateral interactions in more complex systems, whereas a much small number of high accuracy electronic structure calculations would be required to accurately determine the on-site and shortest-ranged interactions. With the present thesis as basis, it remains to future studies to further explore this.